OPTICAL PUMPING OF THE POSITIVE COLUMN OF A HELIUM DC DISCHARGE

W. B. Hurt

Research Associate

Southwest Center for Advanced Studies
Dallas, Texas
U. S. A.

and

C. B. Collins

Assistant Professor

Southwest Center for Advanced Studies
Dallas, Texas
U. S. A.

Presented at

Seventh International Conference on Phenomena in Ionized Gases
Belgrade, Yugoslavia
August 30 - September 4, 1965

This work was supported by the National Aeronautics and Space Administration under grant NsG-269-62

[redacted]

OPTICAL PUMPING OF THE POSITIVE COLUMN
OF A HELIUM DC DISCHARGE

by

W. B. Hurt and C. B. Collins
Southwest Center for Advanced Studies
Dallas, Texas

ABSTRACT

OPTICAL PUMPING OF THE POSITIVE COLUMN
OF A HELIUM DC DISCHARGE

An investigation of the effect of optical pumping on the populations of excited species produced in the positive column of a dc helium discharge has produced evidence of a new process for formation of excited helium molecules. The results suggest that the helium atoms in the 2^3P level undergo a reaction with one or more ground-state atoms to produce excited helium molecular states. This does not, however, appear to be the process responsible for the selective population of the $n = 3$ molecular levels in the positive column of a dc discharge.

[redacted]

1. INTRODUCTION

It is generally unrecognized that the source of helium molecular radiation in the positive column of a dc discharge is unknown. This is due, in part to the fact that it has attracted little attention since the positive column is a weak source of molecular radiation, and in part to the apparent logic that it results from electron recombination of the molecular ion as in the case of intense sources of helium molecular radiation, the weaker intensity in the positive column resulting from the lower electron densities and higher electron temperatures found there. There are several reasons for doubting this explanation. The first is, using Bates' /1/ calculations for excited-state populations and reasonable values of the electron density and electron temperature, the calculated molecular populations are four to six orders of magnitude less than the measured populations. Also, in the positive column, bands originating from the n = 3 electronic levels are several times brighter than bands originating from higher quantum levels, while molecular radiation observed in other sources and known to be the result of recombination of the molecular ion does not suggest a selective population of any quantum level. Further, the bands corresponding to transitions from the V = 1 and V = 2 vibrational levels are virtually non-existent in the positive column while these bands are clearly present in the molecular spectra resulting from recombination of the molecular ion. Any one of these reasons is sufficient to cast serious doubt on the idea that the same process responsible for populating the radiating molecular states in the negative glow /2/ or an afterglow /3/ is also responsible for populating these states in the positive column.

The enhancement of the V = 0 vibrational state of the n = 3 electronic levels suggests that they may be selectively populated by a collision between an atom in a state with energy close to that of the n = 3 molecular states and one or two other ground-state atoms. With a dissociation energy of 2 ev for the helium molecular ion the 2^3P atomic level lies closest to the n = 3 molecular levels. This observation has led to an attempt to vary the population of 2^3P atoms in a positive column without affecting other parameters and to note, if any, a corresponding variation in the intensity of radiation from the n = 3 molecular levels.

2. APPARATUS

Since the 2^3P atomic level is optically connected to the metastable 2^3S level, optical pumping was chosen as the best method to alter the 2^3P population while having the least effect on any of the other parameters likely to effect the molecular intensity.

Figure 1 shows the cell in which the molecular intensity and atomic populations were observed, the water jacket which was filled with different dyes to pass only certain spectral regions of the pumping light, and the coiled pumping tube which was the source of pumping light. In use, the cell and water jacket were positioned along the axis and inside the pumping tube coil as shown. Light shields were placed over both ends of the cell and adjacent to the water jacket in order to prevent any of the pumping tube radiation from reaching the spectrometer entrance slit. Checks on the effect of scattered radiation from the pumping tube were made on all phases of the experiment and in no case was the scattered radiation found to have more than an insignificant effect.

Both the cell and the pumping tube were the positive column of dc discharges in helium. The pumping tube was generally operated at lower pressures than the cell since the atomic radiation was more intense at the lower pressures. The action of cataphoresis served to remove any impurities that may have been in either the cell or pumping tube. However in order to insure purity, data was taken only under conditions in which helium molecular radiation dominated the negative glow, as this is the first feature to disappear when impurities are added to a helium dc discharge.

A photoelectric, 0.5 meter, scanning spectrometer and a helium Pflucker tube were positioned at opposite ends of the cell and a chopper wheel was placed between the Pflucker tube and one end of the cell. With this arrangement the population of atomic and molecular levels radiatiating in the visible could be monitored by measuring the dc signal from the spectrometer photomultiplier (EMI 6256B) and the populations of the 2^1S, 2^1P, 2^3S and 2^3P atomic levels could be monitored by phase-sensitive detection of the chopped 5016Å, 4921Å, 3889Å, and 4471Å radiation from the Pflucker tube. The 1.08 micron radiation was detected with a cooled RCA 7102 photomultiplier tube.

Conversion of the values of fractional absorption as measured by phase sensitive detection to values of $k_o l$ were made, as discussed by Mitchell and Zemansky /4/. The ratio of the Pflucker tube Doppler width to the cell Doppler width was determined from the 4650Å rotational temperatures of the Pflucker tube and cell. For the results presented here these temperatures were 650°K and 540°K for the Pflucker tube and cell respectively and the ratio of the Doppler widths, α, was 1.12. A table of fractional absorption for values of $k_o l$ ranging from 0 to 4.0 and α = 1.12 was calculated on an IBM 1401 computer and the values of $k_o l$ reported here were obtained from that table.

3. RESULTS

With either air or water in the water jacket the effect of the pumping radiation was generally to enchance the populations of those levels optically connected to the atomic metastable states and leave the remaining atomic populations unaltered. In addition to this normal behavior it was found that each of the molecular bands examined also exhibited an increase in population on application of the pumping radiation. This increase ranged from 10% to 25% of the original population depending on the current in the cell with less than 1% of this increase being attributable to scattered molecular radiation from the pumping source. The bands examined represented transitions from both the singlet and triplet series and the n = 3 and n = 4 electronic levels. For a constant cell current and constant pumping intensity no significant difference in the per cent enhancement could be detected for any of the bands examined. In addition, each of the rotational lines of the 4650Å band ($3p\,^3\Pi_g \rightarrow 2s\,^3\Sigma_u^+$) up to J = 19 exhibited similar pumping behavior.

In order to isolate that part of the pumping spectrum responsible for the observed molecular enhancement various liquid filters were used in the water jacket. Tables I and II present the results of observations on the $3p\,^3\Pi_g$ and 2^3P populations obtained using a black dye and a 5% solution of $CuCl_2$ with a cell current and pressure of 11 m.a. and 17 Torr, respectively. Table I lists the transmittance of the black dye filter relative to the transmittance of water at different wavelengths. The black dye effectively filters out all wavelengths except the region around 1 micron (the wavelengths above 1.4 microns are filtered out by the water in the dye). As seen from this table when the 1 micron portion of the pumping radiation was reduced to 71% of its original intensity by the black dye, the enhancements, induced by the filtered pumping radiation, of the 2^3P population and the molecular populations were reduced to 88% and 82%, respectively, of their original values.

Table II lists the results obtained when the black dye is replaced by a 5% solution of CuCl in the water jacket. The effect of the $CuCl_2$ is to selectively filter out the red and infrared portions of the pumping radiation. When the 1 micron region of the pumping radiation was reduced to 3.6% of its original intensity by the $CuCl_2$ solution, the 2^3P population and molecular population enhancements induced by the pumping radiation were reduced to less than 3.7% and 4.6%, respectively, of their original values. This result alone denies the possibility that the 4650Å band enhancement is the result of absorption and reradiation of the $2s\,^3\Sigma_u^+$ molecule. In addition it is doubtful the molecular component of the pumping radiation is sufficiently intense to enhance the population of any of the levels optically connected to the $2s\,^3\Sigma_u^+$ metastable molecule.

The information from these two tables demonstrates that it is the infrared portion of the pumping radiation that is responsible for the enhancement of the molecular population, and indicates that there is a correlation between the molecular intensities and the 2^3P population.

Further evidence for such a correlation is presented in Figure 2 where the 4650Å band intensity is plotted versus the 2^3P population. The range of obtainable 2^3P populations was limited by the extent to which the pumping radiation could increase the ambient 2^3P population in the cell. Within experimental accuracy the data points lie on a straight line that does not extrapolate through zero. Similar data was taken for various cell discharge parameters and different molecular levels and rotational lines with results similar to that presented in Figure 2. The value of the intercept did appear to vary when the cell discharge parameters were altered.

4. DISCUSSION AND CONCLUSION

The results presented in Table I, Table II and Figure 2 indicate a definite correlation between the helium 2^3P population in the positive column and the production of helium molecular levels. Although it may be felt the absorption of the infrared bands by the $2s\,^3\Sigma_u^+$ molecule may in some way enhance all of the molecular levels this explanation has been discarded because the pumping radiation is composed primarily of atomic lines and also it is not consistent with the straight line obtained in Figure 2.

The non-zero intercept obtained in Figure 2 indicates that a process independent of the 2^3P atoms is also important in the positive column. This process cannot be the recombination of molecular ions for the reasons cited in the Introduction.

A tentative explanation for the molecular radiation in the positive column that is consistent, at least qualitatively, with the observed results is as follows. The fraction of the molecular population that is independent of the 2^3P population may result from electron excitation of the $2s\,^3\Sigma_u^+$ metastable molecule. The remaining fraction must result directly or indirectly from the 2^3P atoms. For a molecular ion dissociation energy of 2 ev the n = 3 molecular levels lie closest to the 2^3P energy level and a reaction of the type

$$He(2^3P) + 2He(1^1S) \rightarrow He_2^*(n=3) + He(1^1S)$$

could lead to the conversion of 2^3P atoms to molecules in one or more of the n = 3 electronic levels. Electron collisions could then distribute a fraction of the molecules produced in this way to the remaining n = 3 and higher electronic levels. The above reaction requires a third body by virtue of the "hump" in Mullikan's /5/ recent potential curve for 2^3P and 1^1S helium atoms. The third body provides an additional interaction which may allow the "hump" to disappear as the third body is brought sufficiently close to a colliding pair of 2^3P and 2^1S atoms. Mullikan's curves, as also this interpretation, are dependent on the value of the dissociation energy of the helium molecular ion. This explanation is offerred more as a guide for further experimental investigation rather than a final report on the production of helium molecular radiation in the positive column.

ACKNOWLEDGEMENT

This research was supported by the National Aeronautics and Space Administration under contract NsG-269-62.

5. REFERENCES

1. D. R. Bates, Planet. Space Sci., 11, 1 (1963).

2. W. B. Hurt and W. W. Robertson, J. Chem. Phys., 42, 556 (1965).

3. C. B. Collins, W. B. Hurt and W. W. Robertson, Proc. Third International Conference on Physics of Electronics and Atomic Physics, London (1963) and also C. B. Collins and W. W. Robertson, J. Chem. Phys., 40, 2208 (1964).

4. A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms (Cambridge University Press, London, 1961).

5. R. S. Mullikan, Phys. Rev., 136, A962 (1964).

6. FIGURE CAPTIONS

Figure 1: Cell and Pumping Tube.

Figure 2: Molecular Intensity versus $[2^3P]$.

TABLE I

EFFECT OF BLACK DYE

Wavelength (Å)	Transmittance
10830	.714
7065	.093
6678	.041
5875	.014
5016	.018
4713	.019
4471	.020
4026	.021
3889	.021
3448	.030

$$\frac{\Delta[2^3P]\ (\text{black dye})}{\Delta[2^3P]\ (\text{water})} = .883$$

$$\frac{\Delta I_m\ (\text{black dye})}{\Delta I_m\ (\text{water})} = .821$$

TABLE II

EFFECT OF 5% $CuCl_2$ SOLUTION

Wavelength (Å)	Transmittance
10830	.036
7065	.023
6678	.026
5875	.438
5016	.962
4713	.971
4471	.980
4026	.893
3889	.787
3448	.139

$$\frac{\Delta[2^3P]\ (CuCl_2)}{\Delta[2^3P]\ (\text{water})} < .037$$

$$\frac{\Delta I_m\ (CuCl_2)}{\Delta I_m\ (\text{water})} < .046$$

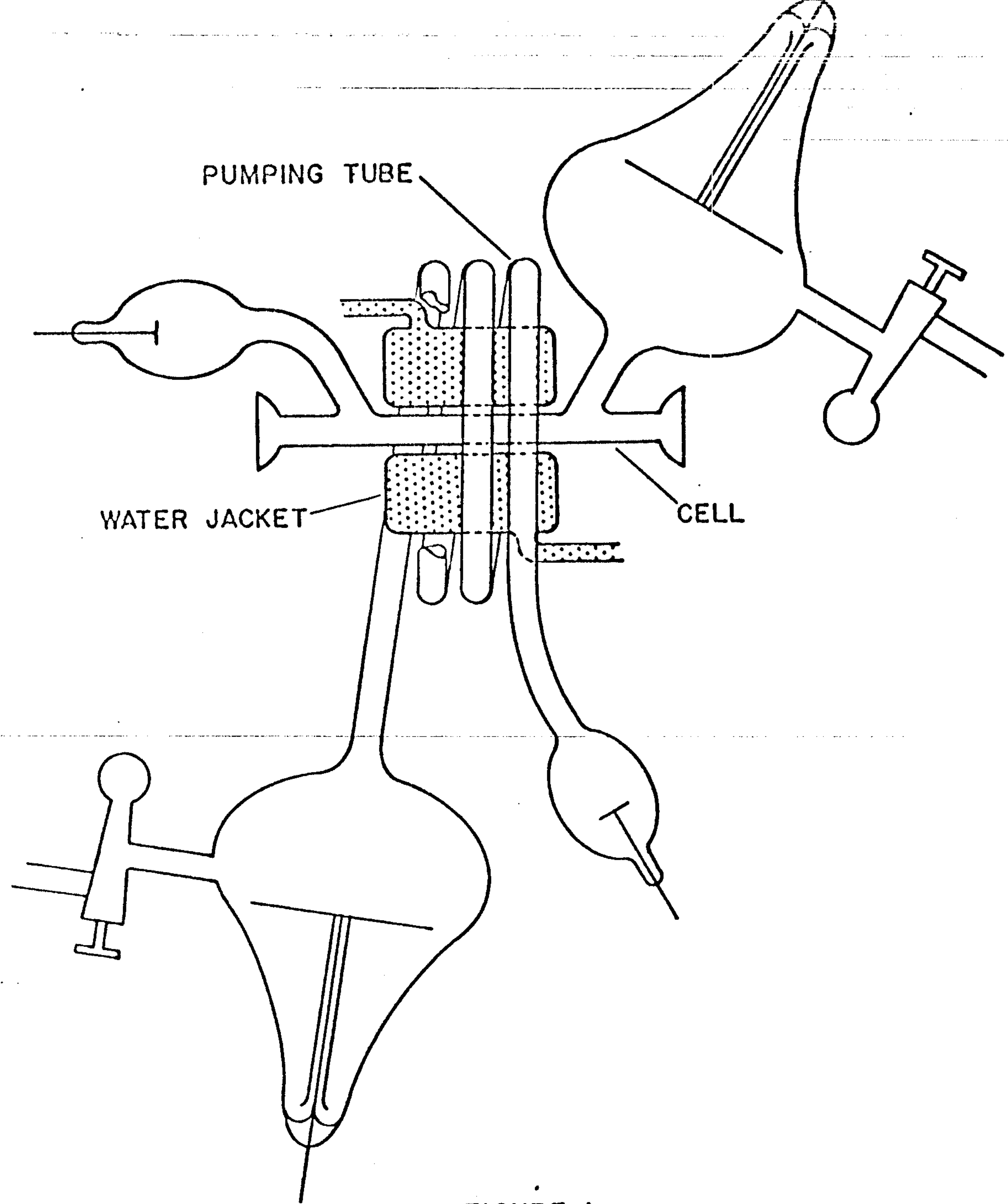

FIGURE 1.
CELL & PUMPING TUBE

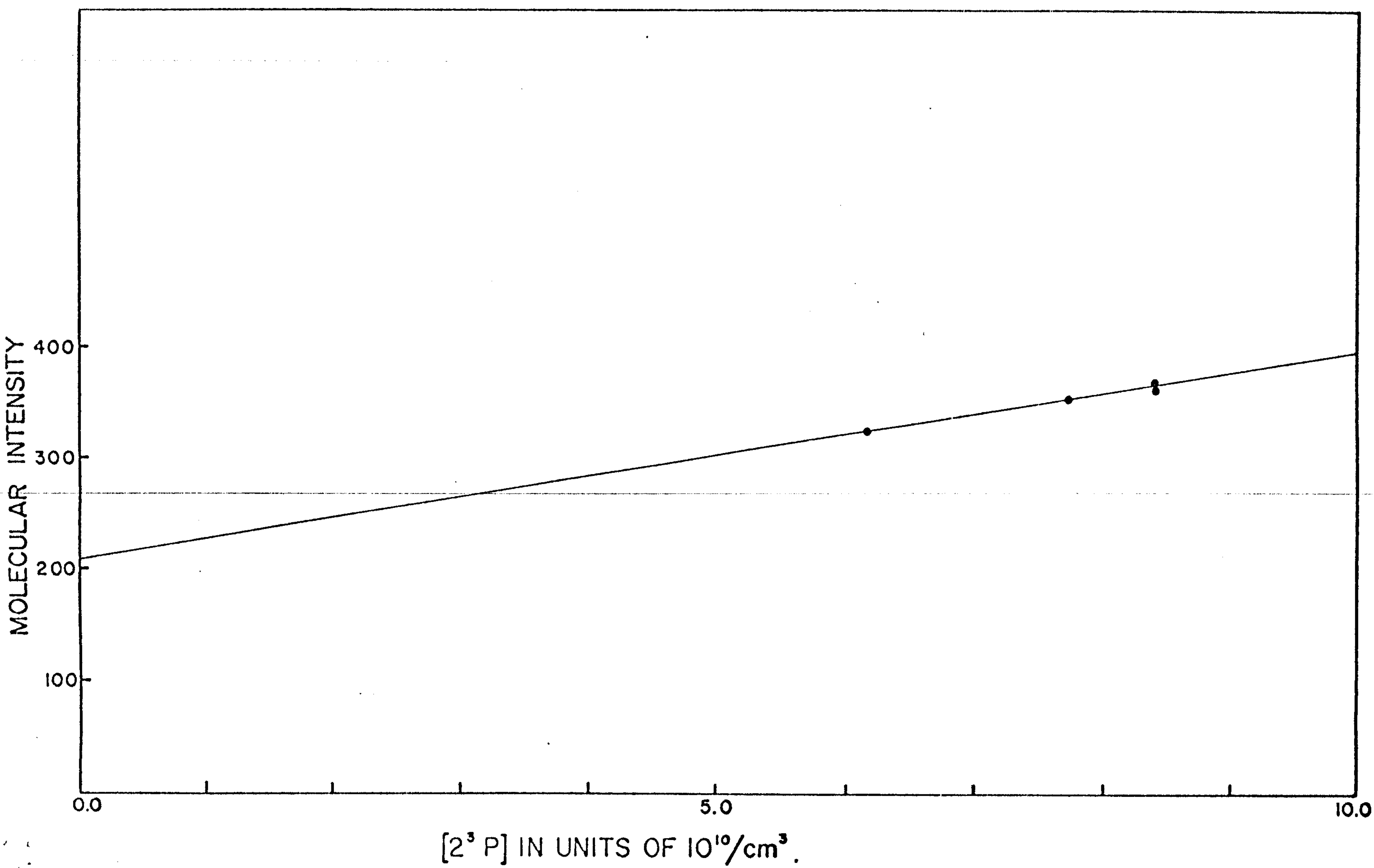
MOLECULAR INTENSITY
100
200
300
400
0.0
5.0
10.0
[2³ P] IN UNITS OF 10¹⁰/cm³.

FIGURE 2